Neutral Mass Spectrometry for Venus Atmosphere and Surface

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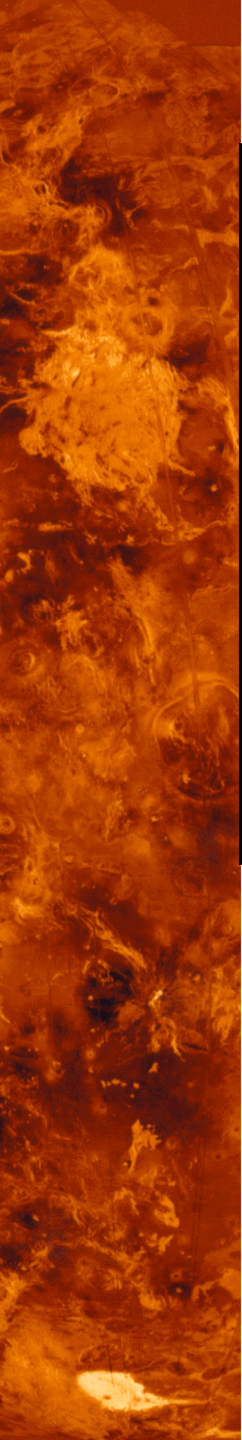
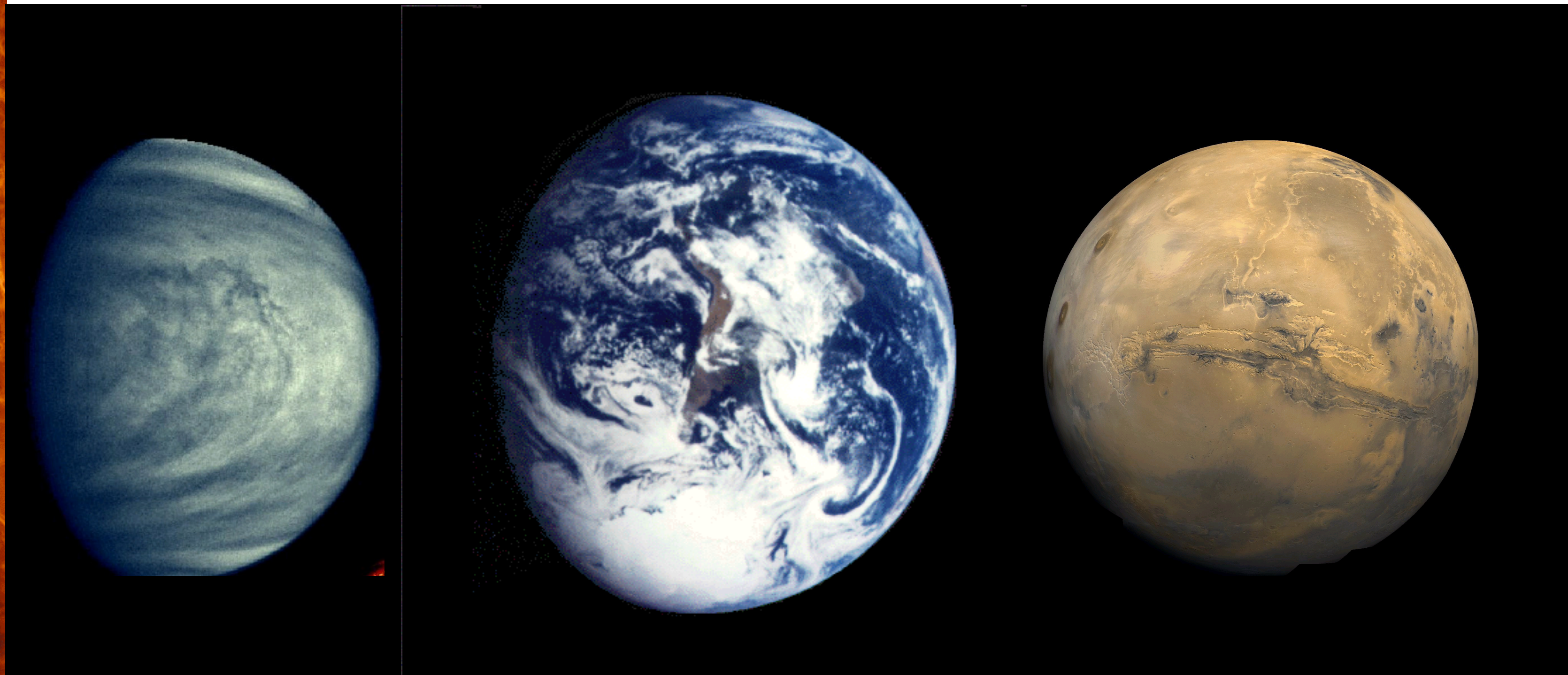


Why such divergent evolution in terrestrial planets?

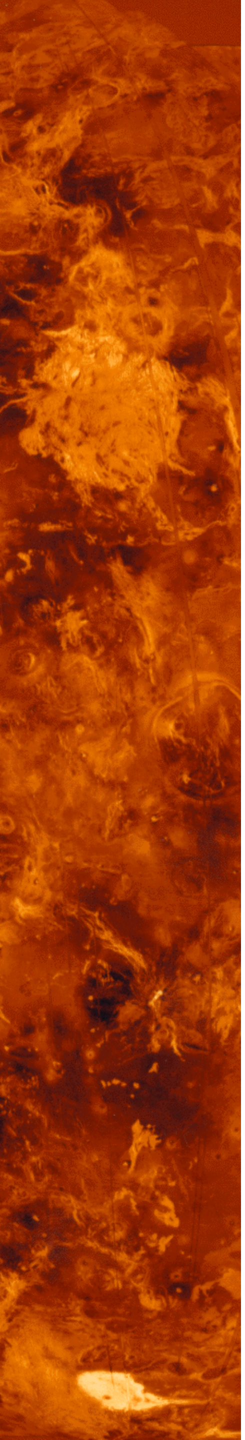


90 bar CO_2
730 K
H_2SO_4 clouds
100,000 x drier than Earth
D/H 160 x Earth
(Venus once wet?)
Thermochemistry below clouds

1 bar N_2, O_2
300 K in San Francisco
Receives ½ the solar radiation of Venus
H_2O clouds
Oceans, Life

7 mbar CO2
~210 K
H_2O and CO_2 ice clouds
D/H 5 x Earth
Photochemistry at surface

How unique is our solar system?



Motivation for improved mass spectrometer measurements at Venus

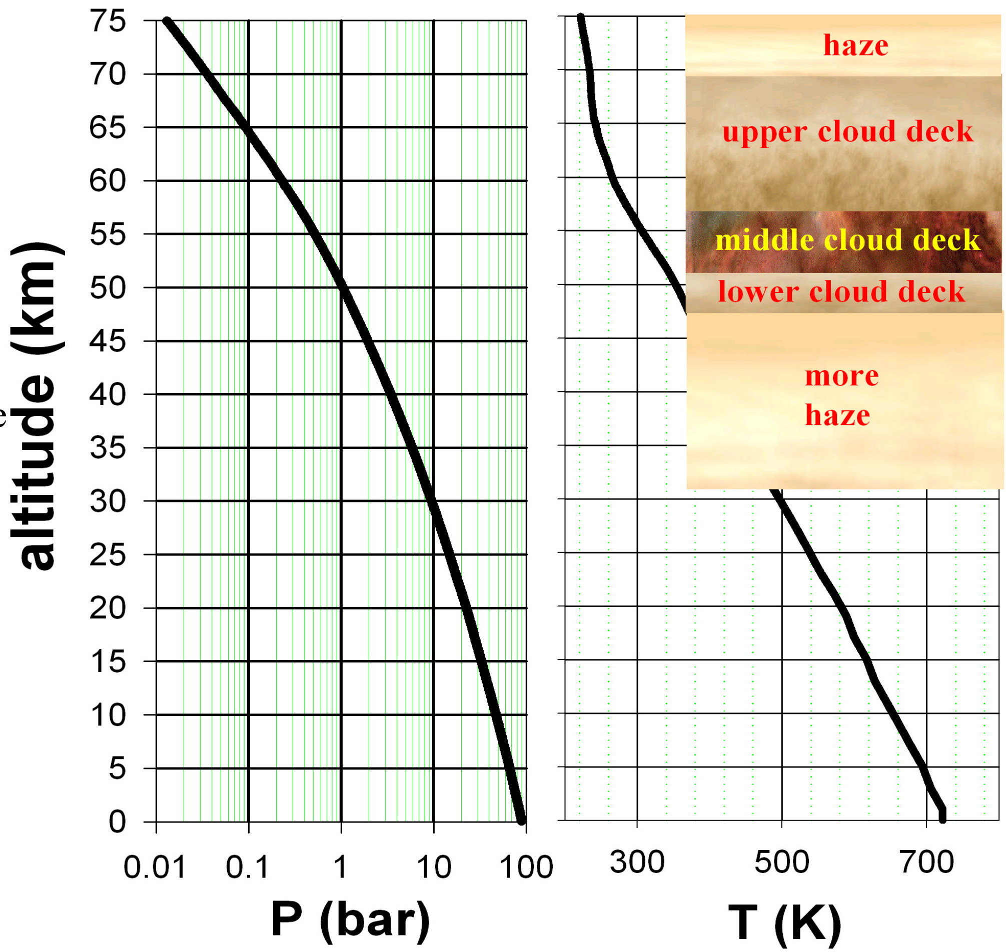
- to address fundamental issues of terrestrial planetary formation and evolution

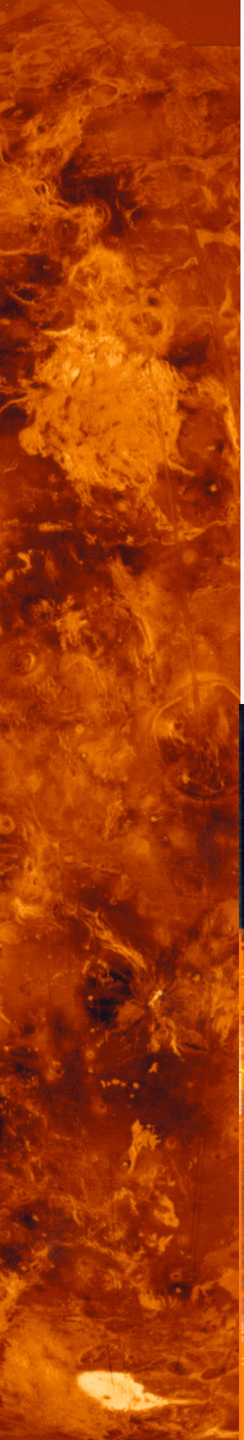
The assignment

- to make precise (better than 1 %) measurements of isotope ratios and accurate (5-10%) measurements of abundances of noble gas
- to obtain vertical profiles of trace chemically active gases from above the clouds all the way down to the surface

The challenge for Venus probe mass spectrometry

- 4 orders of magnitude pressure differential on track from above clouds to surface
- trace species measured to parts per billion
- 9 orders of magnitude difference between atmospheric pressure at surface and ion source pressure in mass spectrometer
- 500 degree temperature gradient from atmosphere above clouds to surface
- cloud droplets and aerosols that can clog mass spectrometer inlet systems and mask real vertical variations due to their condensation on surfaces
- a fast ride to the surface with an entry probe





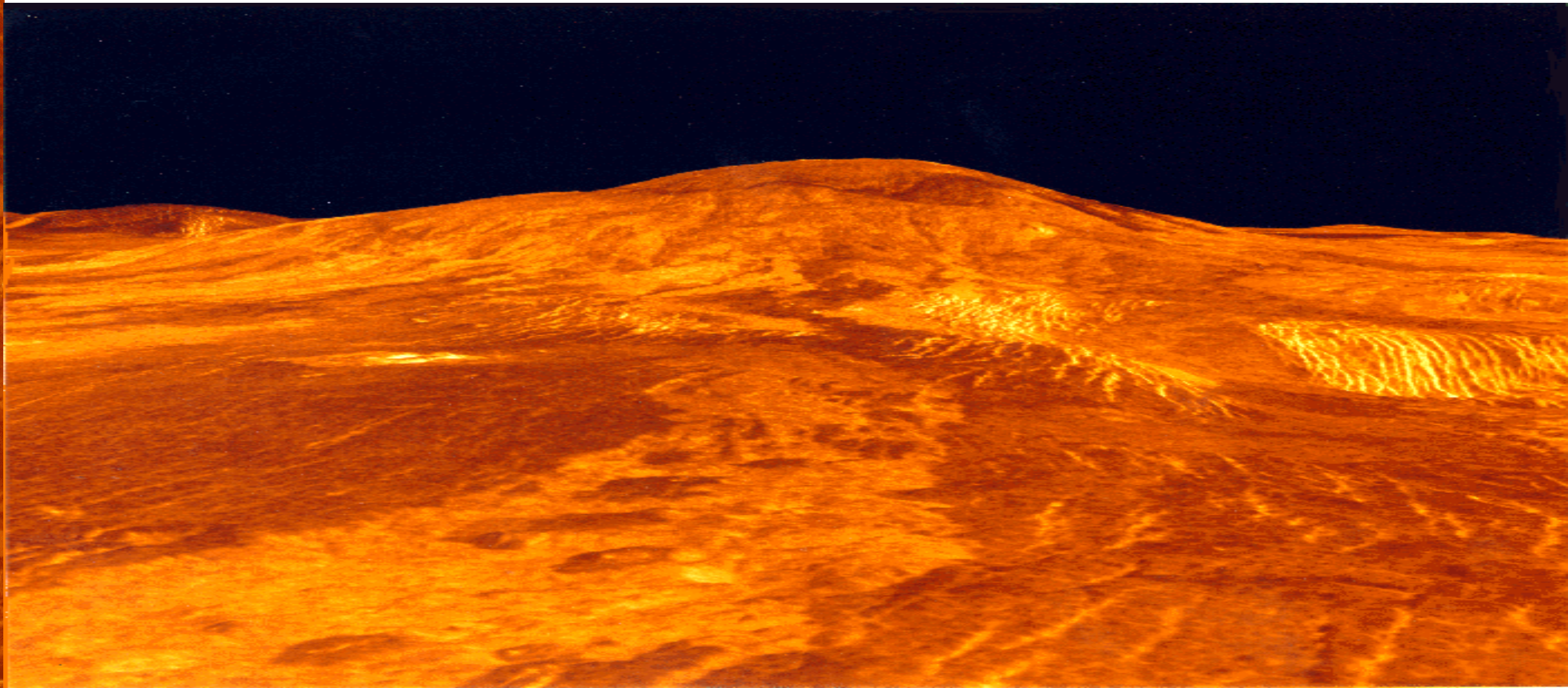
Topics

Near term Venus science goals for chemical and isotopic measurements

Where have the Venus missions, to date, left us with respect to these goals?

- noble gas elemental and isotopic composition
- cloud chemistry
- surface science

The challenge of Venus mass spectrometry and future directions



Science goals - atmosphere & surface chemical & isotope measurements

Space Studies Board SSE Strategy – July 2002

- **The first billion years of solar system history**

    1. What processes marked the initial stages of planet and satellite formation?
    2. How long did it take Jupiter to form and how did the formation of the gas and ice giants differ?
    3. What was the rate of decrease of impacts by comets, asteroids, and other objects and how did it affect the emergence of life?

- **Volatiles and organics: the stuff of life**

    1. What is the history of volatile material, especially water, in our solar system?
    2. What is the nature and history of organic material in our solar system?
    3. What planetary processes affect the evolution of volatile on planets?

- **The origin and evolution of habitable worlds**

    1. Where are zones in our solar system where like can exist and what are the processes for producing and sustaining habitable planets?
    2. Does (or did) life exist beyond the Earth?
    3. Why did Mercury, Venus, Earth, and Mars diverge so much in their evolution?
    4. What hazards do solar system objects present to Earth?

- **How planets work**

    1. How do the processes that shape planets today operate and interact?
    2. What does our solar system tell us about other solar systems?

Decadal Study Recommendations for Venus

Profile

Venus In Situ Explorer

Mission Type: Lander

Cost Class: Medium

Priority Measurements:

- Determine elemental and mineralogical surface compositions.
- Measure the composition of the atmospheres, especially trace gases and their isotopes.
- Undertake high-precision measurements of noble gases and light stable isotopes.
- Assess processes and rates of atmosphere-surface interaction.
- Search for evidence of volcanic gases in inner-planet atmospheres.

Decadal Study Themes and Science Questions for Terrestrial Planets

Guiding Themes Addressed	Important Planetary Science Questions Addressed
Volatiles and Organics The Stuff of Life	*What global mechanisms affect the evolution of volatiles on planetary bodies?* *What is the history of water on the inner planets?* *How did the atmospheres of the inner planets evolve?*
The Origin and Evolution of Habitable Worlds	*Why have the terrestrial planets differed so dramatically in their evolution?* *What kinds of minerals are the inner planets made of, and does this vary depending on a planet's distance from the Sun?*
Processes How Planetary Systems Work	*How do the processes that shape the contemporary character of planetary bodies operate and interact?* *What processes stabilize climate?* *How do planets' varied geological histories enable predictions of volacanic and tectonic activity?*

Science measurement objectives of VISE are as follows:

- Determine the composition of Venus' atmosphere, including trace gas species and light stable isotopes
- Accurately measure noble-gas isotopic abundance in the atmosphere
- Provide descent, surface, and ascent meteorological data
- Measure zonal cloud-level winds over several Earth days
- Obtain near-IR descent images of the surface from 10-km altitude to the surface
- Accurately measure elemental abundances & mineralogy of a core from the surface
- Evaluate the texture of surface materials to constrain weathering environment.

Motivation for noble gas measurements at Venus

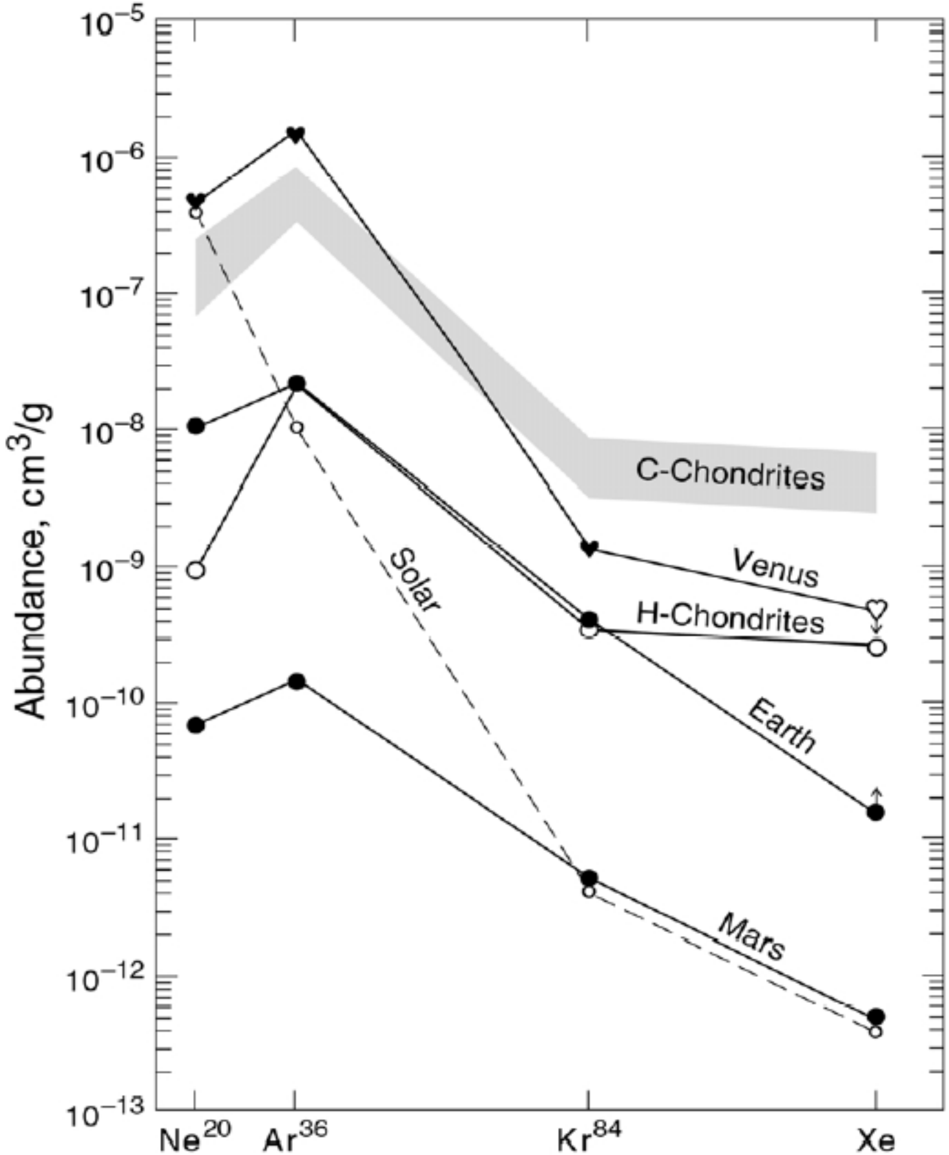
Noble gas elemental ratios and isotopic fractionation constrain models of atmospheric formation and evolution

Noble gas elemental ratios

Inner planet noble gas elemental abundances do not match those of the sun or various types of chondrites.

The $^{36}Ar/^{84}Kr$ ratio at Venus may be much more solar like than Earth or Mars.

However - great uncertainty in Kr and Xe elemental abundances



From Owen and Bar-Num, Orig. of Life and the Evolution of the Biosphere, 31, 435, 2001.

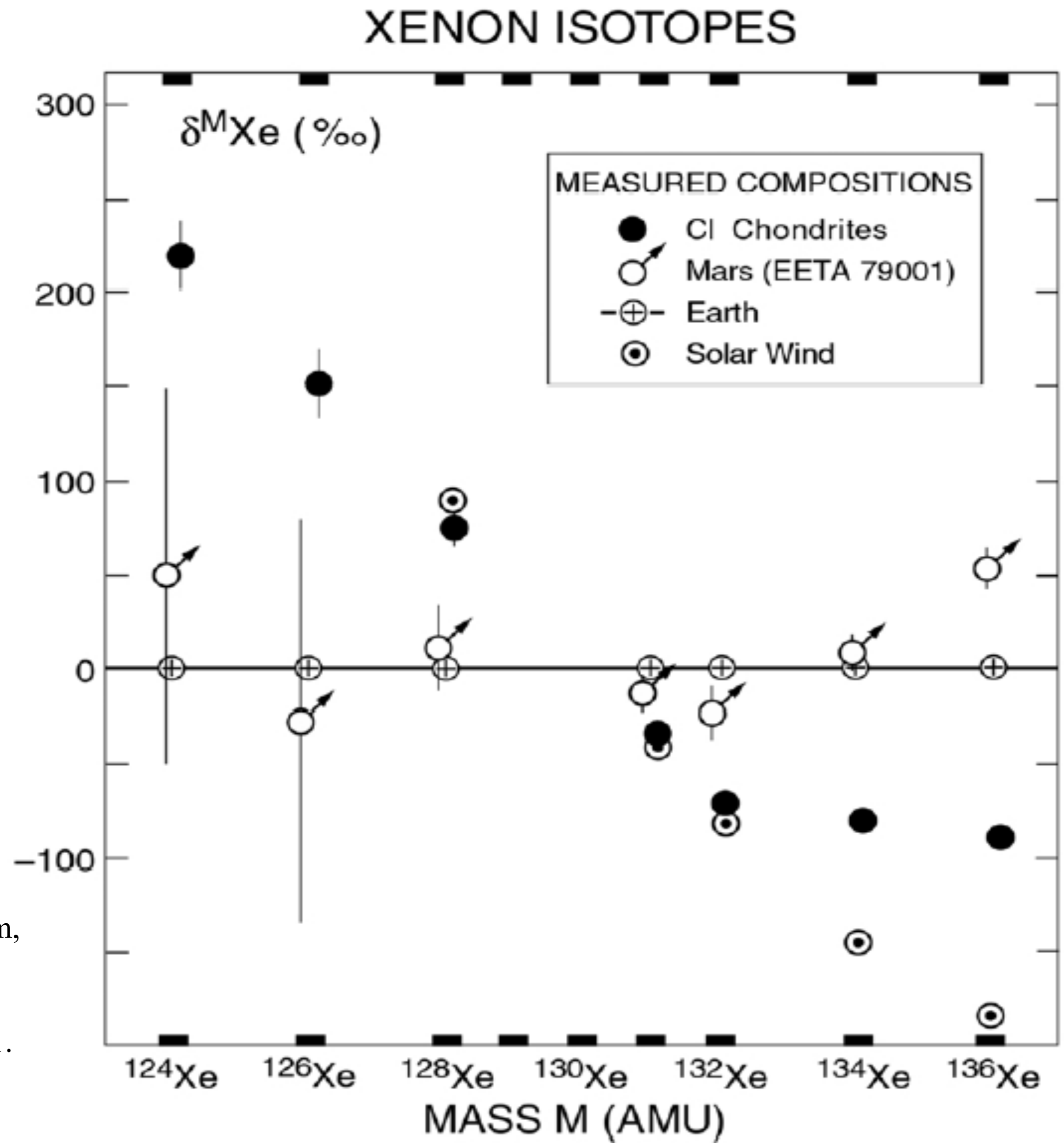
Xenon Isotopic Composition

Mars and Venus vs. the Sun and chondrites.

The Martian values are established from SNC meteorite analysis.

The fractionation in Venus is unknown.

If fractionation on Venus was found to be similar to Earth and Mars, then fractionation could have occurred in planetesimals prior to their incorporation in planets



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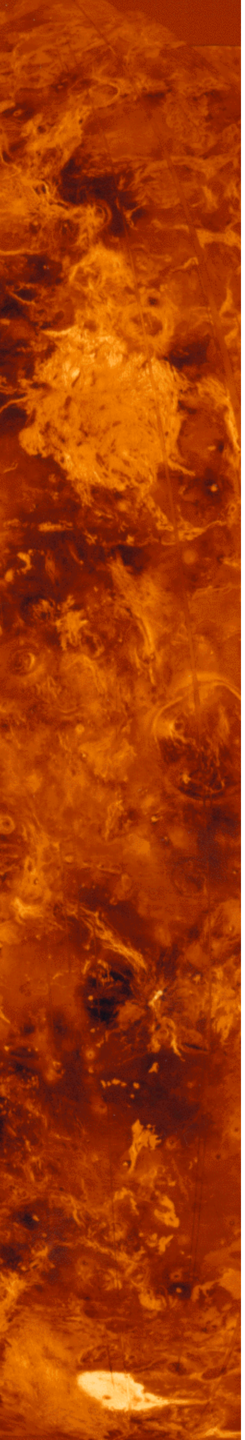
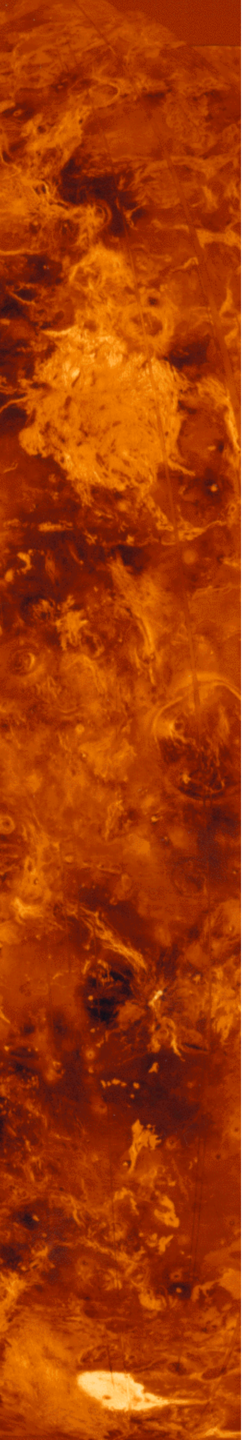


Current status of noble gas measurements at Venus

Xe – no isotope information, upper limit on abundance
Kr – no isotope information, great uncertainty in abundance



Present state of the art in Venus noble gas measurements

Noble gas abundance	**Previous measurements**	**notes**
He	12 (+24,-8) ppm	extrapolated from meas. > 130 km
Ne	7 $\pm$ 3 ppm	4 MS measurements
Ar	70 $\pm$ 25 ppm	3 MS and 2 GC measurements
Kr	0.4 $\pm$ 0.14	Venera 11 and 12 reproduced measurements
	0.2	PV Probe Hoffman analysis
	0.025	PV Probe Donahue analysis
Xe	0.12 upper limit	PV Probe Donahue analysis

Target accuracy <5-10%

Noble gas isotope ratio	**Previous measurement**	**notes**
$^{3}He/^{4}He$	---	^{3}He predicted at low ppb level – methane or H_2 could give H_3^+ interference with HD
$^{20}Ne/^{22}Ne$	11.8 $\pm$ 0.7	Potential interference from $^{40}Ar^{++}$ at 20 Da and CO_2^{++} at 22 Da
$^{20}Ne/^{21}Ne$	---	
$^{36}Ar/^{38}Ar$	5.56 $\pm$ 0.62	PV Probe Donahue analysis
	5.08 $\pm$ 0.05	Venera 11/12 MS
$^{40}Ar/^{36}Ar$	1.03 $\pm$ 0.04	PV Probe Donahue analysis
	1.19 $\pm$ 0.07	Venera 11/12 MS
Kr isotopes	---	
Xe isotopes	---	

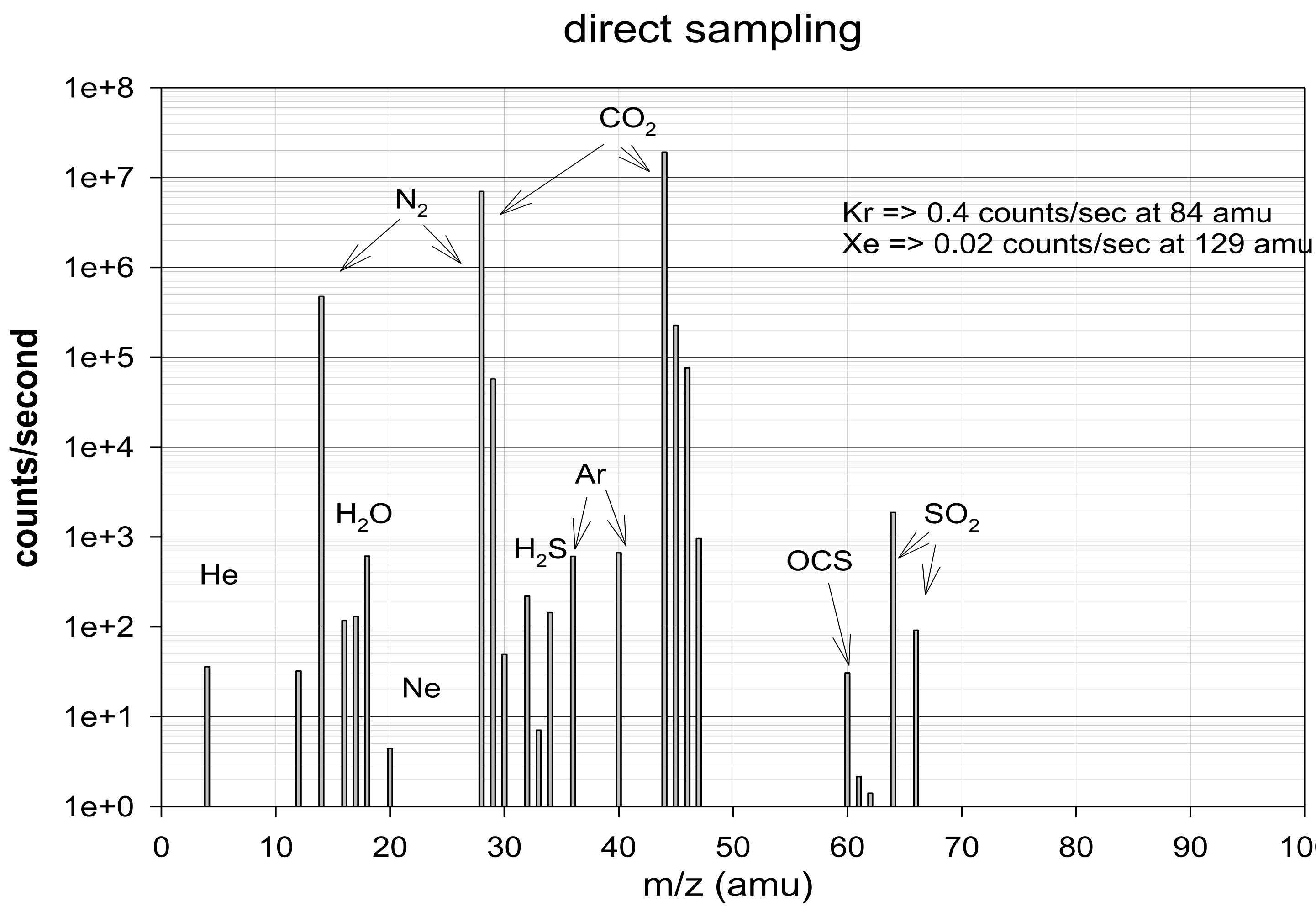
Target precision <1-2%

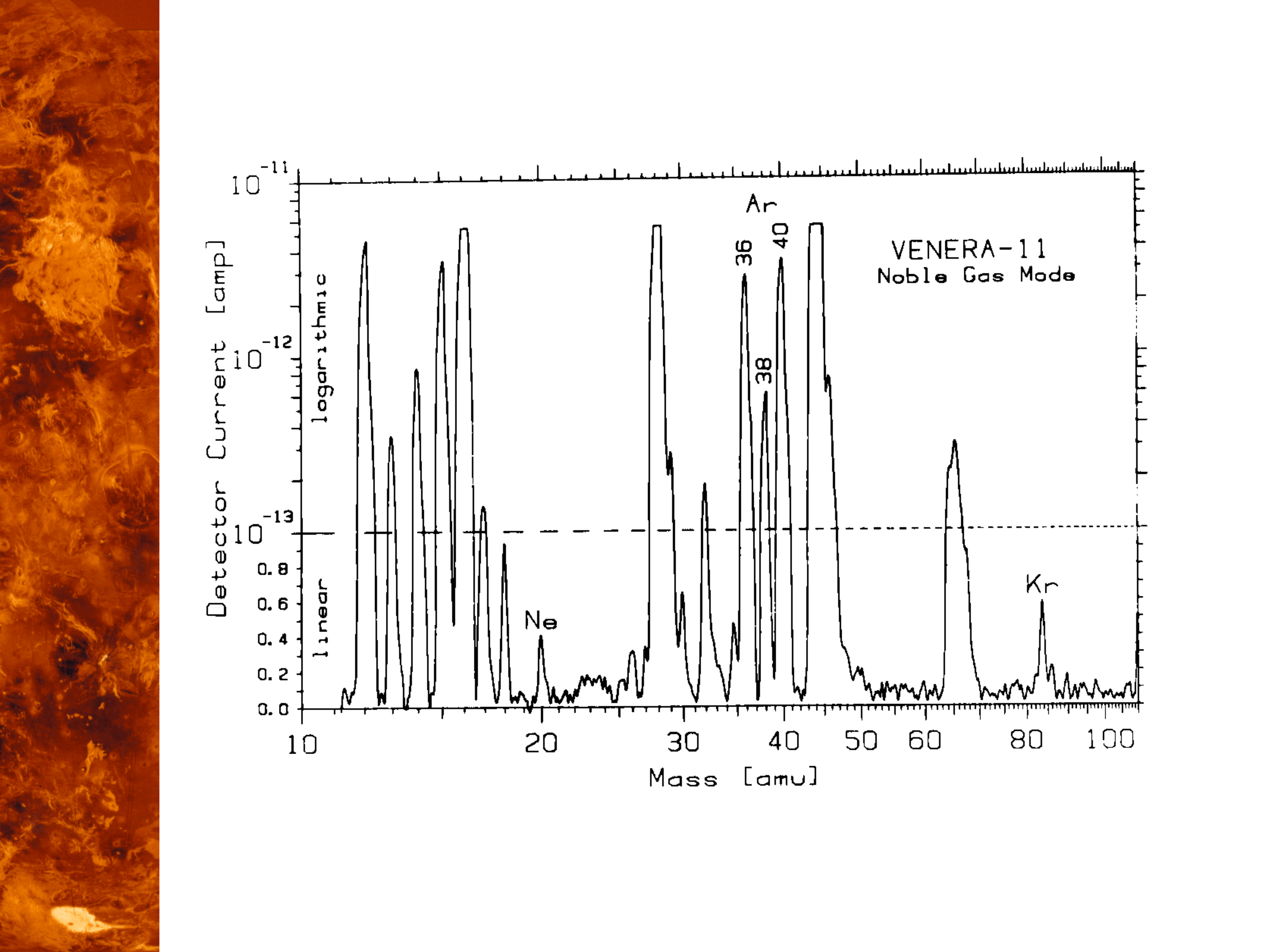
Key future measurements → Kr and Xe abundance and isotopic distribution

Approach for future noble gas measurements at Venus

Wide dynamic range mass spectrometer
Dedicated noble gas processing unit to optimize all noble gas measurements including Xe and Kr

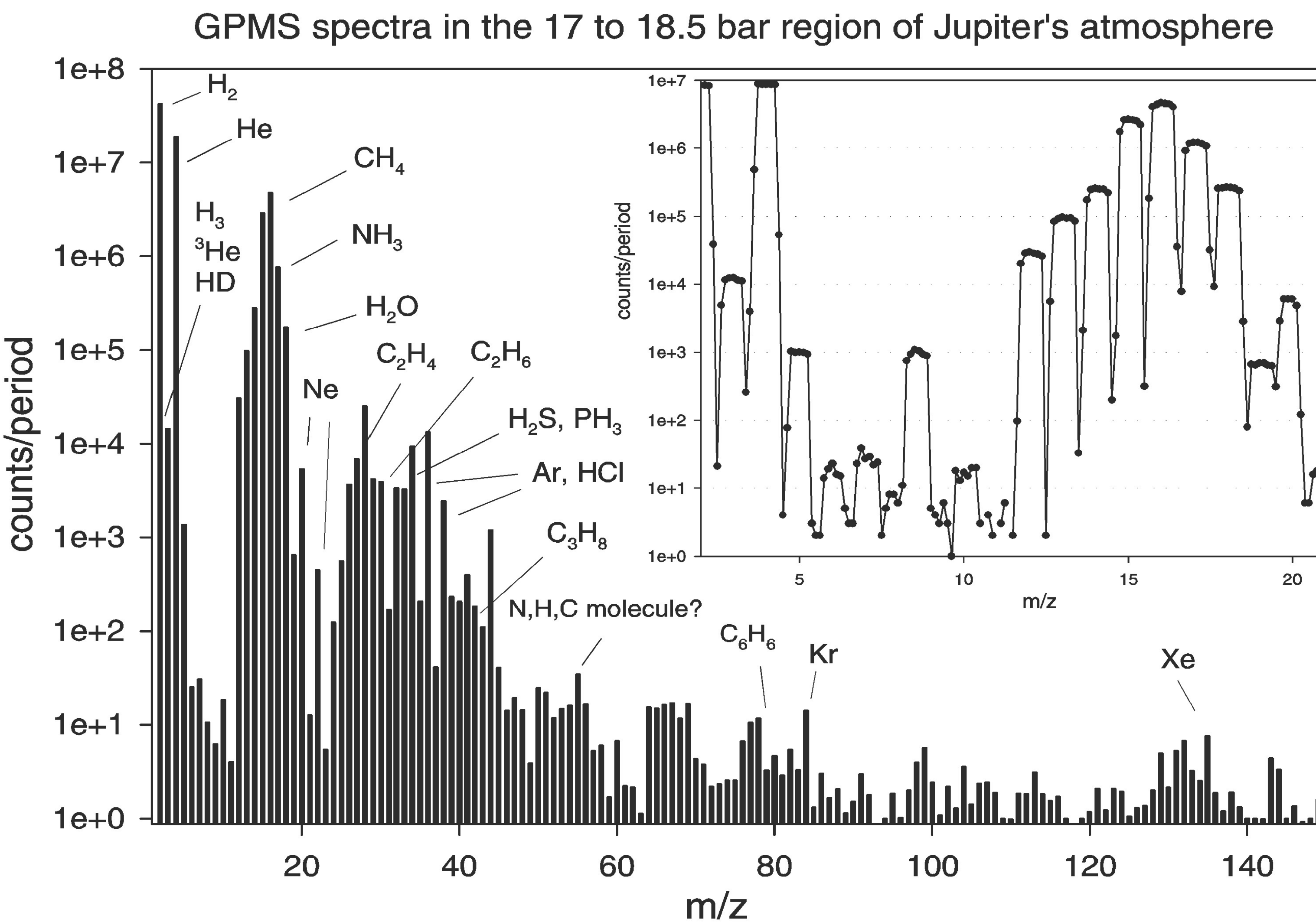
Predicted signal with direct sampling at Venus with no enrichment or saturation of CO_2



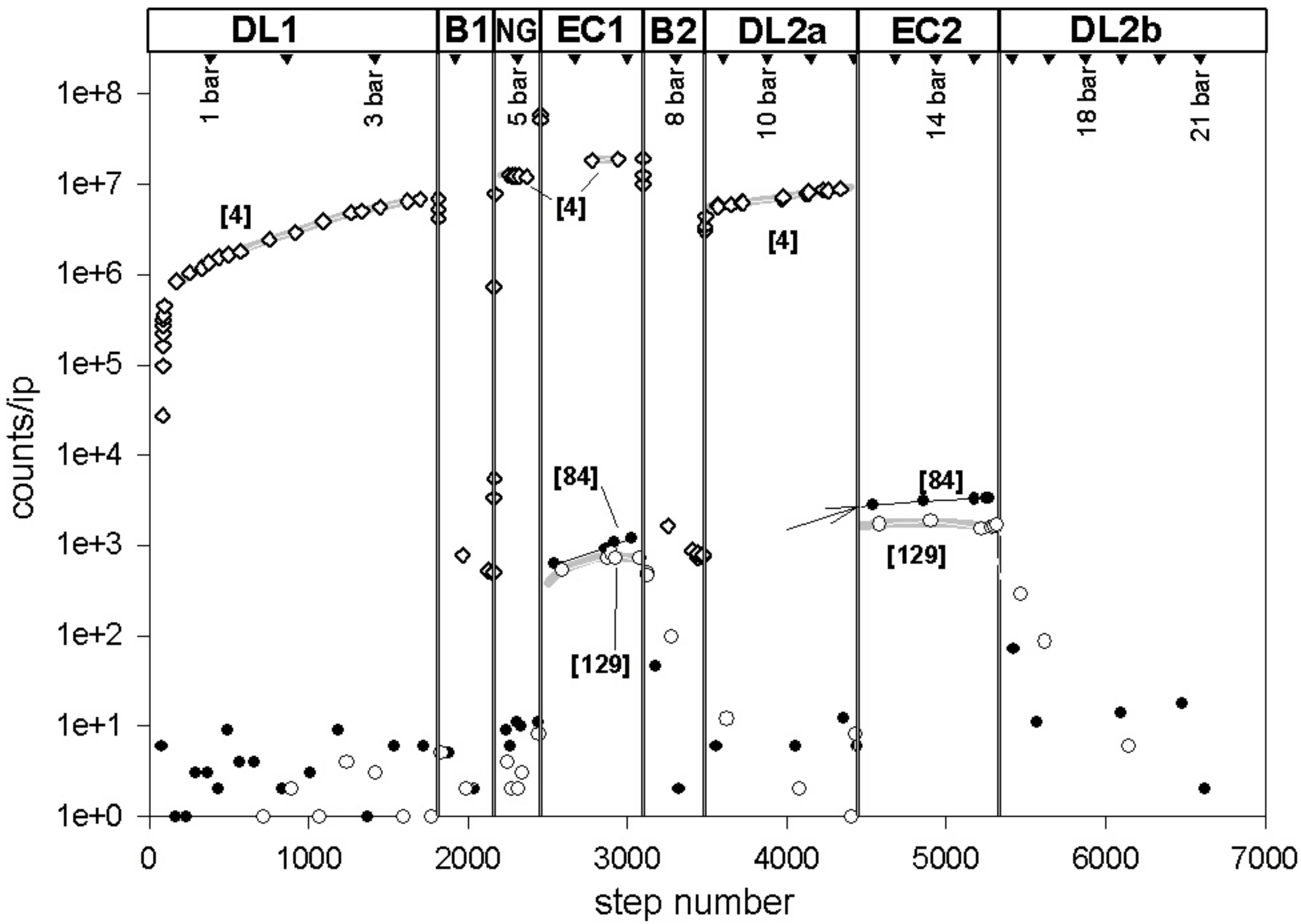


VENERA-11
Noble Gas Mode
Ar
36
38
40
Ne
Kr
Detector Current [amp]
logarithmic
linear
10^{-11}
10^{-12}
10^{-13}
0.8
0.6
0.4
0.2
0.0
10
20
30
40
50
60
80
100
Mass [amu]

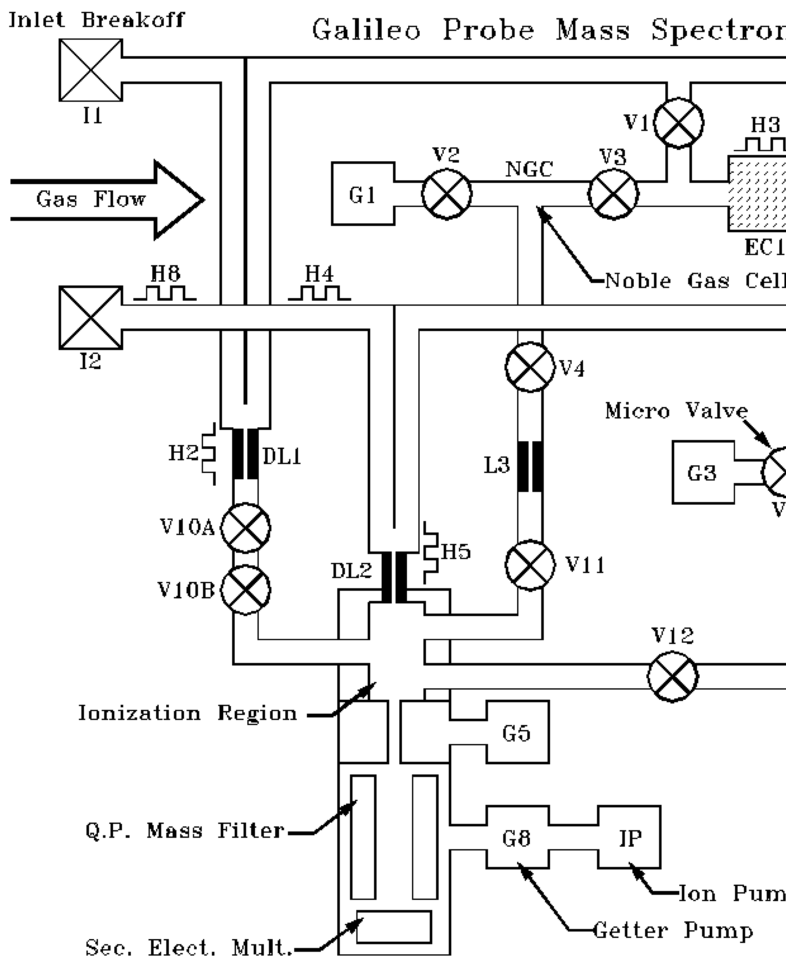
Dynamic range possible with small quadrupole mass spectrometer

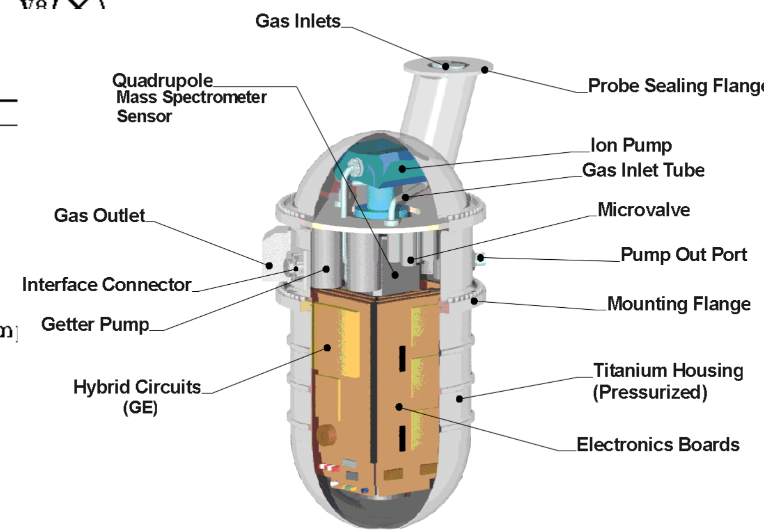


Galileo Probe use enrichment but NOT static MS

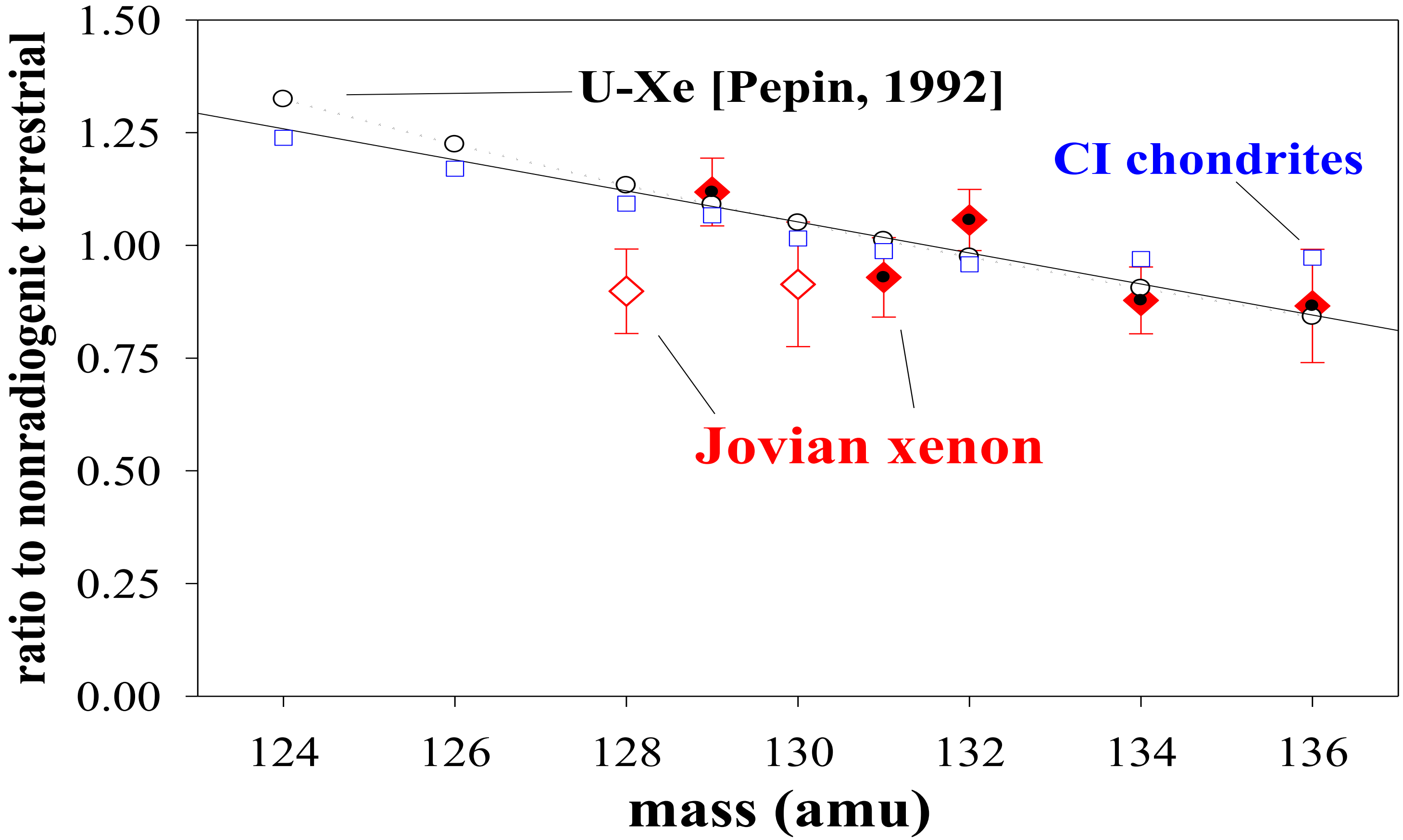


Enrichment techniques – the Galileo Probe Neutral Mass Spectrometer approach





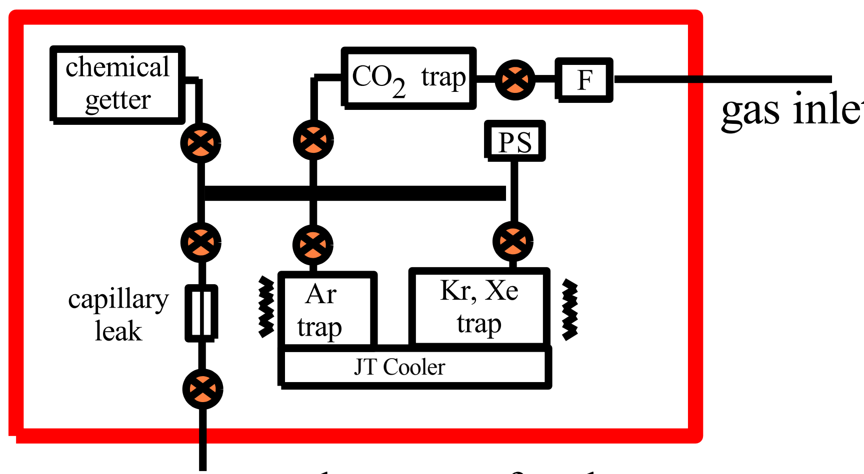
Xenon Isotopic Fractionation at Jupiter from the Galileo Probe Mass Spectrometer



A proposed measurement protocol for Venus noble gas and $^{15}N/^{14}N$ measurement

- sample a volume of Venus atmospheric gas
- chemically remove CO_2 as gas is sampled
  (for example, $CaO\ (s) + CO_2(g) \rightarrow CaCO_3\ (s)$)
- $(^{15}N^{14}N)/^{14}N_2$ with dynamic MS to obtain $^{15}N/^{14}N$
- chemically remove N_2 and other active gases with a getter
- cryogenically remove Kr and Xe (on high surface area trap)
- $^{38}Ar/^{36}Ar$ and $^{36}Ar/^{40}Ar$ with static MS
- cryogenically remove Ar
- residual $^{20}Ne/^{22}Ne$ and $^{21}Ne/^{22}Ne$ and $^{3}He/^{4}He$ with static MS
- release Kr and Xe
- all Kr and Xe isotopes with static MS

gas separation system

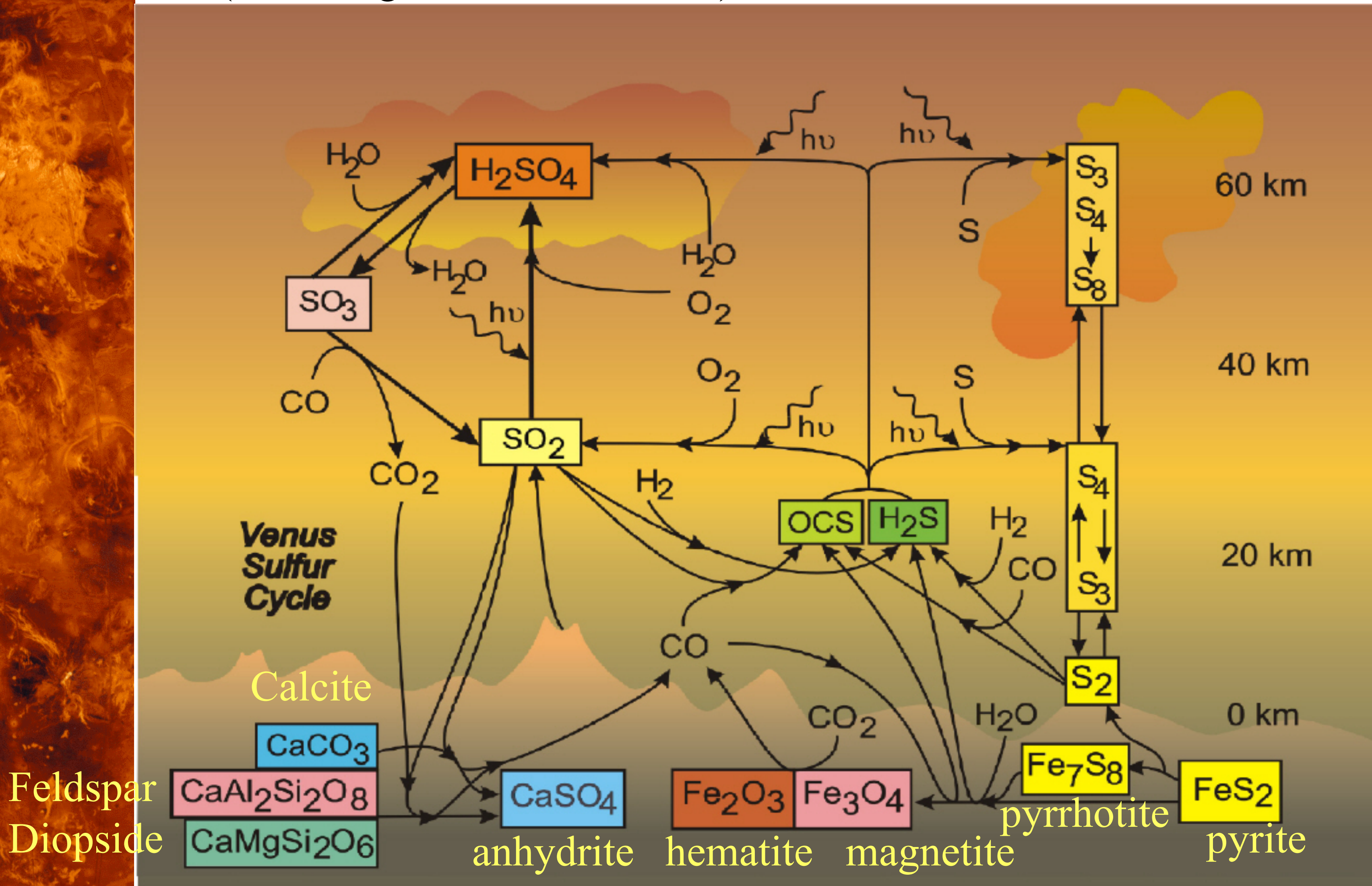


processed gas transfered to static or dynamic MS

Motivation for trace gas measurements at Venus

Vertical profiles through the clouds and down to the surface enable cloud chemistry and atmosphere/surface interactions to be studied

S cycle - B. Fegley et al., in Venus II, U. AZ Press, 618 (1997) (following van Zahn & Prinn).



Gases and reactions expected to be important for cloud chemistry

SO_2, H_2O, SO_3 , SO, OCS

$$SO_2 + \tfrac{1}{2}\,O_2 + H_2O + M \rightarrow H_2SO_4$$ net reaction

Photolysis of $SO_2 \rightarrow SO + O$

Elemental sulfur

$SO + SO \rightarrow SO_2 + S$

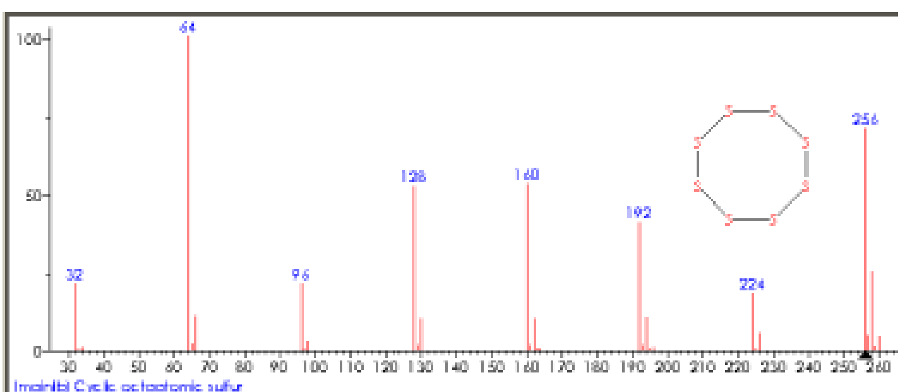
$S + S + M \rightarrow S_2 + M$

$S_2 + S_2 + M \rightarrow S_4 + M$

$S_4 + S_4 + M \rightarrow S_8 + M$

Other possible species

NO, Cl_2, S_2Cl_2 etc



Reactions that may be important for surface/atmosphere interaction

Volcanoes likely source of SO_2

Weathering of surface minerals may buffer atmospheric gases

$CaCO_3(s) + SO_2(g) \rightarrow CaSO_4(s) + CO(g)$

Calcite anhydrite

(time constant ~ 2 M yr – Fegley & Prinn, 1989)

$CaCO_3\ (s) + SiO_2\ (s) = CaSiO_3\ (s) + CO_2\ (g)$

Calcite quartz wollastonite

(source of calcite – Fegley & Treiman, 1992)

Trace species of interest that reflect the oxidation state near the surface

H_2S, SO_2, OCS, O_2, CO, H_2O

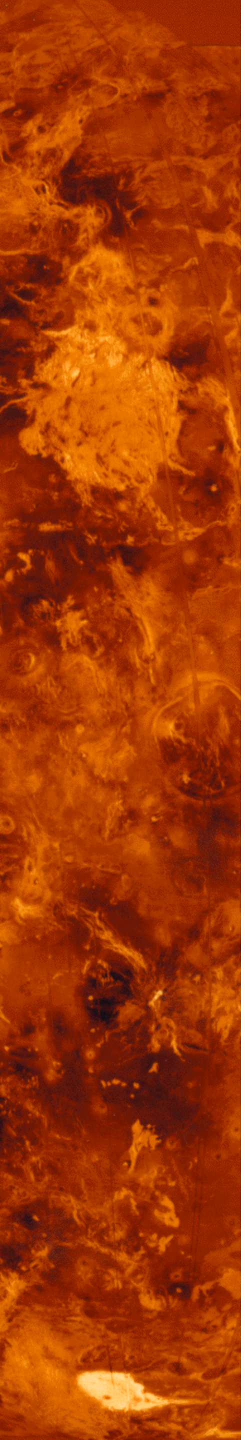
Oxidation state determines Fe mineralogy

$Fe_3O_4(s) + O_2 = Fe_2O_3\ (s)$

magnetite hematite

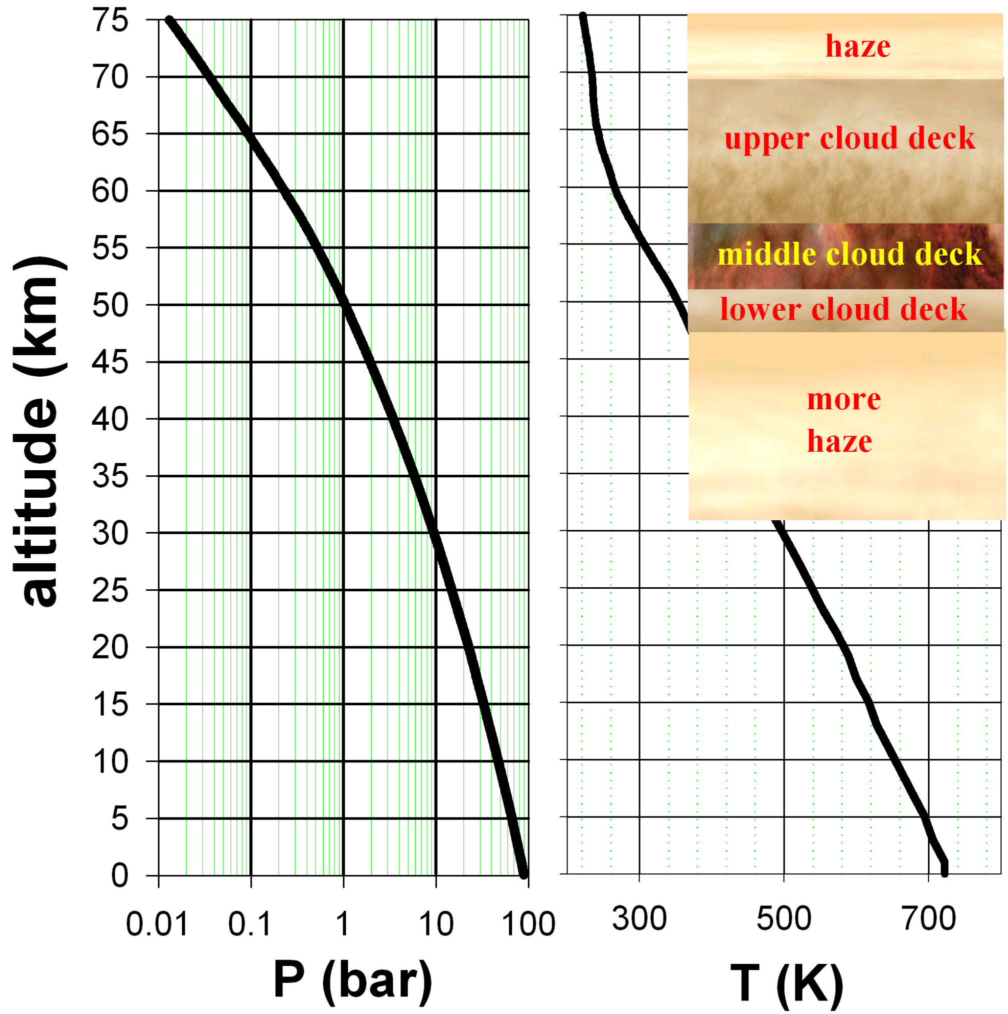
Past and future Venus mass spectrometer experiments

Need to address the difficult sampling issues



Sampling issues

- 4 orders of magnitude pressure differential on track from above clouds to surface
- trace species measured to parts per billion
- 9 orders of magnitude difference between atmospheric pressure at surface and ion source pressure in mass spectrometer
- 500 degree temperature gradient from atmosphere above clouds to surface
- cloud droplets and aerosols that can clog mass spectrometer inlet systems and mask real vertical variations due to their condensation on surfaces



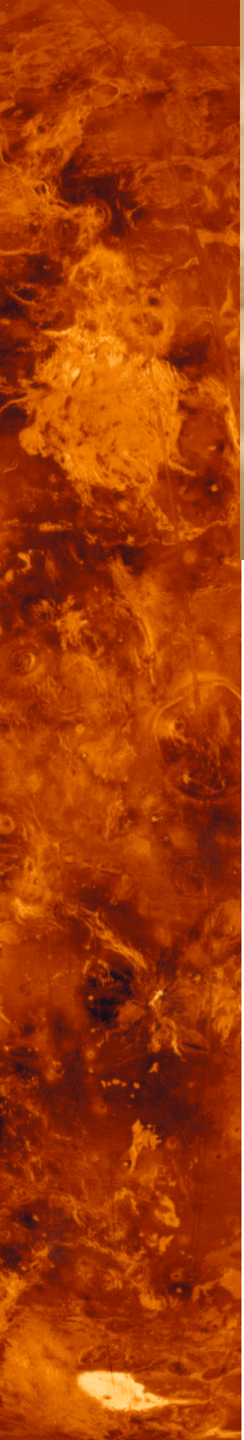
Example Venus mass spectrometer experiments

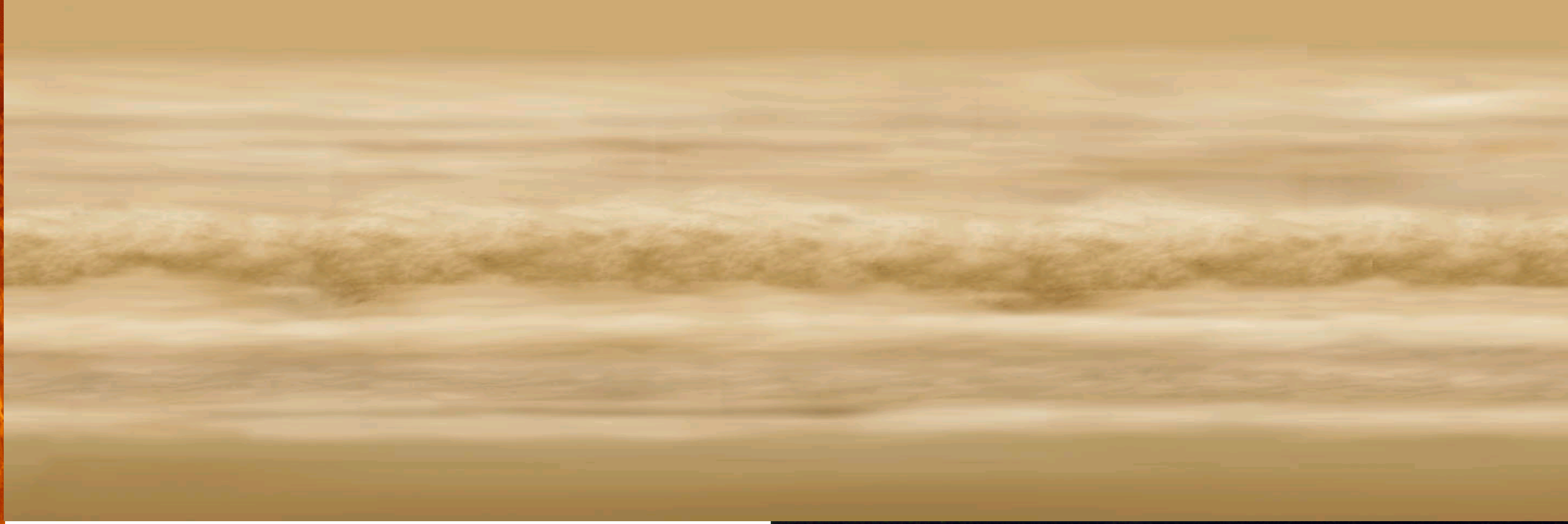
Mission (Team, Date)	Mass Spectrometer	Altitude (Pressure)	Inlet type	Outcome
Venera 9 & 10 (Surkov, von Zahn, 1975)	monopole	63-34 km (130 mbar to 6 bar	3 porous plugs	instrument measured primarily background signal throughout descent
PV-Large Probe (Hoffman, 1978)	magnetic sector	62 km to surface	pinched Ta tube (3 inlets)	50 km to 29 km inlet was blocked and instrument measured outgassing from H_2SO_4 droplets
Venera 11 & 12 Lander (Grechnev, 1978)	Bennett RF	23 km to surface	1 m x 5 mm inlet pipe & pulsed microvalve	possible inlet tube memory effects, Ar isotopes in "static" mode, Kr detected but isotopes NOT resolved
PV-Orbiter (Niemann, Kasprzak, 1978-1992)	Quadrupole MS	orbiter (upper atmosphere)	source open to ambient	14 years of data →neutral scale heights (CO_{+}, CO, N_2, O, N, and He) O escape (thermospheric measurements gave no information on heavy noble gas isotopes)
PV-Multiprobe Bus (von Zahn, 1978)	Magnetic Sector	entry to 0.01 mbar	open with differential P	entry measurements (upper limit on ^{36}Ar and ^{40}Ar), identified He homopause at 137 km

Atmospheric sampling approach

- short inlet lines heated above ambient to vaporize condensates
- chemically inert materials in inlet
- adequate aerosol traps and baffles
- multiple inlet leaks
- redundant inlet lines

TEST
TEST
TEST
TEST





The future of Venus exploration?

- near term objectives from the planetary science community are clearly recommended to NASA in the Decadal Study Report
- the probe/measurement technology is ready for noble gas and trace species measurements
- NASA Discovery & New Frontier Missions may enable some of these recommendations to be realized
- future Venus detailed cloud investigations, long term surface packages and sample return clearly require advanced technology support